

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
15 July 2004 (15.07.2004)

PCT

(10) International Publication Number  
**WO 2004/058878 A1**

(51) International Patent Classification<sup>7</sup>: **C08L 23/04**,  
C08F 297/08

Rainer [DE/DE]; Augustaanlage 26, 68165 Mannheim  
(DE).

(21) International Application Number:  
PCT/EP2003/013975

(74) Agent: **HOFFMANN, Peter**; Basell Polyolefine GmbH,  
Industriepark Höchst, Intellectual Property, Building E413,  
65926 Frankfurt am Main (DE).

(22) International Filing Date:  
10 December 2003 (10.12.2003)

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,  
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,  
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
102 61 065.7 24 December 2002 (24.12.2002) DE  
60/445,164 5 February 2003 (05.02.2003) US

(84) Designated States (*regional*): ARIPO patent (BW, GH,  
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,  
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BERTHOLD**,  
Joachim [DE/DE]; Am Flachsland 54, 65779 Kelkheim  
(DE). **BÖHM**, Ludwig [DE/DE]; Leonhardstrasse 36,  
65795 Hattersheim (DE). **KRÜMPEL**, Peter [DE/DE];  
Hopfenstrasse 6, 65520 Bad Camberg (DE). **MANTEL**,

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: POLYETHYLENE BLOW MOLDING COMPOSITION FOR PRODUCING LARGE CONTAINERS

(57) Abstract: The invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for the blow molding of large containers with a volume in the range of from 10 to 150 dm<sup>3</sup> (l). The composition has a density in the range of from 0.949 to 0.955g/cm<sup>3</sup> at 23 °C and an MFI<sub>190/5</sub> in the range of from 0.1 to 0.3 dg/min. It comprises from 38 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 30 to 40 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C.



WO 2004/058878 A1

Title: Polyethylene blow molding composition for producing large containers

5 The present invention relates to a polyethylene blow molding composition with multimodal molecular mass distribution, which is particularly suitable for blow molding of large blow moldings with a capacity in the range from 10 to 150 dm<sup>3</sup> (l), and to a process for preparing this blow molding composition in the presence of a catalytic system composed of a Ziegler catalyst and a co-catalyst like triethylaluminum, triisobutylaluminum, alkylaluminumchlorides and  
10 alkylaluminumhydrides, by way of a multistage reaction process composed of successive slurry polymerizations. The invention further relates to large containers produced from the blow molding composition by injection blow molding.

15 Polyethylene is widely used for producing blow moldings of all types requiring a material with particularly high mechanical strength, high corrosion resistance, and absolutely reliable long-term stability. Another particular advantage of polyethylene is that it also has good chemical resistance and is intrinsically a light-weight material.

20 EP-A-603,935 has previously described a blow molding composition based on polyethylene and having a bimodal molecular mass distribution, and suitable for the production of moldings with good mechanical properties.

25 US-A 5,338,589 describes a material with even broader molecular mass distribution, prepared using a high-mileage catalyst known from WO 91/18934, in which the magnesium alcoholate is used in the form of a gel-like suspension. Surprisingly, it has been found that the use of this material in moldings permits simultaneous improvement in properties which are usually contrary correlated  
30 in semicrystalline thermoplastics, these being stiffness on the one hand and stress-crack resistance and toughness on the other hand.

However, the known bimodal products, in particular, have relatively low melt strength during processing. This means that the extruded parisons frequently break in the molten state, making the extrusion process unacceptably sensitive to processing. In addition, especially when thick-walled containers are being produced, the wall thickness is found to be non-uniform, due to flow of the melt from upper regions into lower regions of the mold.

It is an objective of the present invention, therefore, to develop a polyethylene composition for blow molding which shows a further improvement over all of the known materials in processing by blow molding to produce large blow moldings. In particular, the high melt strength of the composition should permit to run an extrusion process without parison disruption over a long period, and the precisely adjusted swell ratio index of the composition should permit an optimization of wall-thickness control.

15

We have surprisingly found that this objective is achieved by way of a composition as mentioned at the outset, the characterizing features of which are that it comprises from 38 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 30 to 40 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the molding composition.

25 The invention also relates to a process for preparing this composition in a cascaded slurry polymerization and to a process for producing, from this composition, large containers with a capacity (volume) in the range from 10 to 150 dm<sup>3</sup> (l) and with quite excellent mechanical properties.

30 The polyethylene composition of the invention has a density in the range of from 0.949 to 0.955 g/cm<sup>3</sup> at 23 °C, and a broad trimodal molecular mass distribution. The high-molecular-mass copolymer B contains only small

amounts of other 1-olefins having from 4 to 8 carbon atoms, namely from 0.1 to 0.2 % by weight. Examples of these co-monomers are 1-butene, 1-pentene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The ultrahigh-molecular-mass ethylene homo- or copolymer C also contains an amount in the range from 2 to 3 % by weight of one or more of the above mentioned co-monomers.

The polymer composition of the invention has a melt flow index ISO 1133 in the range of from 0.1 to 0.3 dg/min, expressed in terms of  $MFI_{190/5}$ , and in the range of from 4 to 6 dg/min, expressed in terms of  $MFR_{190/21.6}$ , and a viscosity number  $VN_{tot}$  in the range of from 460 to 500  $cm^3/g$  measured to ISO/R 1191 in decalin at 135 °C.

The trimodality is a measure of the position of the centers of gravity of the three individual molecular mass distributions, and can be described with the aid of the viscosity number VN to ISO/R 1191 of the polymers formed in the successive polymerization stages. The relevant band widths for the polymers formed in each of the stages of the reaction are therefore as follows:

The viscosity number  $VN_1$  measured on the polymer after the first polymerization stage is identical with the viscosity number  $VN_A$  of the low-molecular-mass polyethylene A and according to the invention is in the range of from 160 to 220  $cm^3/g$ .

The viscosity number  $VN_2$  measured on the polymer after the second polymerization stage is not equal to  $VN_B$  of the high-molecular-mass polyethylene B formed in the second polymerization stage, which can only be determined by calculation, but rather represents the viscosity number of the mixture of polymer A and polymer B. According to the invention,  $VN_2$  is in the range of from 250 to 300  $cm^3/g$ .

The viscosity number  $VN_3$  measured on the polymer after the third polymerization stage is not equal to  $VN_C$  of the ultra-high-molecular-mass

copolymer C formed in the third polymerization stage, which can only be determined by calculation, but rather represents the viscosity number of the mixture of polymer A, polymer B, and polymer C. According to the invention,  $VN_3$  is in the range from 460 to 500  $\text{cm}^3/\text{g}$ .

5

The polyethylene is obtained by polymerizing the monomers in slurry in a temperature range of from 60 to 90 °C, at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound. The  
10 polymerization is conducted in three stages, i.e. in three stages arranged in series, each molecular mass being regulated with the aid of a hydrogen feed.

The polyethylene composition of the invention may comprise other additives alongside the polyethylene. Examples of these additives are heat stabilizers,  
15 antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds which destroy peroxide, and basic co-stabilizers in amounts of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, and also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistatics, blowing agents, or a combination of these, in total  
20 amounts of from 0 to 50 % by weight, based on the total weight of the mixture.

The composition of the invention is particularly suitable for the blow molding process to produce large containers, by first plastifying the polyethylene composition in an extruder in the temperature range of from 200 to 250 °C and  
25 then extruding it through a die into a mold, where it is blown up and cooled and, thus, solidified.

The composition of the invention gives particularly good processing behavior in the blow molding process to produce large blow moldings, such as large  
30 containers, because it has a swell ratio index in the range of from 175 to 205 %, and the large blow moldings produced therewith have particularly high mechanical strength because the molding composition of the invention has a

notched impact strength (ISO) in the range of from 30 to 60 kJ/m<sup>2</sup>. The stress-crack resistance (FNCT) is in the range of from 60 to 110 h.

5 The notched impact strength<sub>ISO</sub> is measured according to ISO 179-1/1eA / DIN 53453 at 23 °C. The size of the specimen is 10 x 4 x 80 mm, and a V notch is inserted using an angle of 45°, with a depth of 2 mm and with a notch base radius of 0.25 mm.

10 The stress-crack resistance of the molding composition of the invention is determined by an internal test method and is given in h. This laboratory method is described by M. Fleißner in Kunststoffe 77 (1987), pp. 45 et seq., and corresponds to ISO/CD 16770, which has since come into force. The publication shows that there is a relationship between determination of slow crack growth in the creep test on specimens with a circumferential notch and  
15 the brittle section of the long-term internal- and hydrostatic-pressure test to ISO 1167. In ethylene glycol as stress-crack-promoting medium at 80 °C with a tensile stress of 3.5 MPa, the time to failure is shortened due to the shortening of the stress-initiation time by the notch (1.6 mm/razorblade). The specimens are produced by sawing out three specimens of dimensions 10 x 10 mm from a  
20 pressed plaque of thickness 10 mm. These specimens are provided with a central notch, using a razorblade in a notching device specifically manufactured for the purpose (see Figure 5 in the publication). The notch depth is 1.6 mm.

### Example 1

Ethylene was polymerized in a continuous process in three reactors arranged in series. An amount of 1.0 mol/h of a Ziegler catalyst prepared as specified in WO 91/18934, Example 2, and having the operative number 2.2 in the WO,  
5 was fed into the first reactor together with 15 mol/h of triethylaluminum, as well as sufficient amounts of diluent (hexane), ethylene, and hydrogen. The amount of ethylene (= 5.3 t/h) and the amount of hydrogen (= 2.3 kg/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas phase of the first reactor were 33 % by volume and 56 % by volume,  
10 respectively, and the rest was a mix of nitrogen and vaporized diluent.

The polymerization in the first reactor was carried out at 70 °C.

The slurry from the first reactor was then transferred into a second reactor, in  
15 which the percentage proportion of hydrogen in the gas space had been reduced to 16 % by volume, and an amount of 7 kg/h of 1-butene was added to this reactor alongside 4.5 t/h of ethylene. The amount of hydrogen was reduced by way of intermediate H<sub>2</sub> depressurization. 67 % by volume of ethylene, 16 % by volume of hydrogen, and 0.37 % by volume of 1-butene were measured in  
20 the gas phase of the second reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 85 °C.

25 The slurry from the second reactor was transferred to the third reactor using further intermediate H<sub>2</sub> depressurization to adjust the amount of hydrogen to < 0.5 % by volume in the gas phase of the third reactor.

An amount of 69 kg/h of 1-butene was added to the third reactor alongside an  
30 amount of 2.8 t/h of ethylene. A percentage proportion of 87 % by volume of ethylene, < 0.5 % by volume of hydrogen, and 1.25 % by volume of 1-butene

was measured in the gas phase of the third reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the third reactor was carried out at 75 °C.

5

The long-term polymerization catalyst activity required for the cascaded process described above was provided by a high-mileage Ziegler catalyst as described in the WO mentioned at the outset. A measure of the usefulness of this catalyst is its extremely high hydrogen sensitivity and its uniformly high activity over a long time period of from about 1 to 8 h.

10

The diluent is removed from the polymer slurry leaving the third reactor, and the polymer is dried and then pelletized.

15

Table 1 shown below gives the viscosity numbers and quantitative proportions  $w_A$ ,  $w_B$ , and  $w_C$  of polymer A, B, and C for the polyethylene composition prepared in Example 1.

**Table 1**

20

Example	
density [g/cm <sup>3</sup> ]	0.951
MFI <sub>190/5</sub> [dg/min]	0.20
MFR <sub>190/21.6</sub> [dg/min]	4.6
$w_A$ [% by weight]	42
$w_B$ [% by weight]	36
$w_C$ [% by weight]	22
VN <sub>1</sub> [cm <sup>3</sup> /g]	200



VN <sub>2</sub> [cm <sup>3</sup> /g]	270
VN <sub>tot</sub> [cm <sup>3</sup> /g]	480
SR [%]	190
FNCT [h]	80
NIS <sub>ISO</sub> [kJ/m <sup>2</sup> ]	40

The abbreviations for physical properties in Table 1 have the following meanings:

- 5    -    SR (= swell ratio) in [%] measured in a high-pressure capillary rheometer at a shear rate of 1440 s<sup>-1</sup>, in a 2/2 round-section die with conical inlet (angle = 15°) at 190 °C.
- 10    -    FNCT = stress-crack resistance (Full Notch Creep Test) tested using the internal test method of M. Fleißner, in [h],
- 15    -    NIS<sub>ISO</sub> = notched impact strength measured to ISO 179-1/1eA / DIN 53453 in [kJ/m<sup>2</sup>] at 23 °C.

\* \* \* \* \*

We claim

5

1. A polyethylene composition with multimodal molecular mass distribution, which has a density in the range of from 0.949 to 0.955 g/cm<sup>3</sup> at 23 °C and a MFI<sub>190/5</sub> in the range from 0.1 to 0.3 dg/min or a MFI<sub>190/21.6</sub> in the range of 4 to 6 dg/min, and which comprises from 38 to 45 % by weight of  
10 a low-molecular-mass ethylene homopolymer A, from 30 to 40 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the  
15 molding composition.

2. A polyethylene composition as claimed in claim 1, wherein the high-molecular-mass copolymer B contains small proportions of from 0.1 to 0.2 % by weight of co-monomer having from 4 to 8 carbon atoms, based on  
20 the weight of copolymer B, and wherein the ultrahigh-molecular-mass ethylene copolymer C contains an amount in the range from 2 to 3 % by weight of co-monomers, based on the weight of copolymer C.

3. A polyethylene composition as claimed in claim 1 or 2, which, as co-  
25 monomer, contains 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, or a mixture of these.

4. A polyethylene composition as claimed in one or more of claims 1 to 3, which has a viscosity number VN<sub>tot</sub> in the range of from 460 to 500 cm<sup>3</sup>/g  
30 measured to ISO/R 1191 in decalin at 135 °C.

- 5
6. A process for producing a polyethylene composition as claimed in one or more of claims 1 to 5, in which the monomers are polymerized in slurry in a temperature range of from 60 to 90 °C at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound, which comprises conducting polymerization in three stages, where the molecular mass of the polyethylene prepared in each stage is regulated with the aid of hydrogen.
- 10
7. A process as claimed in claim 6, wherein the hydrogen concentration in the first polymerization stage is adjusted so that the viscosity number  $VN_1$  of the low-molecular-weight polyethylene A is in the range of from 160 to 220  $\text{cm}^3/\text{g}$ .
- 15
8. A process as claimed in claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is adjusted so that the viscosity number  $VN_2$  of the mixture of polymer A and polymer B is in the range of from 250 to 300  $\text{cm}^3/\text{g}$ .
- 20
9. A process as claimed in any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is adjusted so that the viscosity number  $VN_3$  of the mixture of polymer A, polymer B, and polymer C is in the range of from 460 to 500  $\text{cm}^3/\text{g}$ .
- 25
10. The use of a polyethylene composition as claimed in one or more of claims 1 to 5 for producing large blow moldings, such as containers, with a capacity in the range of from 10 to 150  $\text{dm}^3$  (l), wherein the polyethylene
- 30

molding composition is first plasticized in an extruder in a temperature range of from 200 to 250 °C and is then extruded through a die into a blow mold, where it is blown up and then cooled and solidified.

\* \* \* \* \*

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08L23/04 C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 45 980 A (ELENAC GMBH) 29 March 2001 (2001-03-29) the whole document	1-10
X	US 4 536 550 A (IKEGAMI TADASHI ET AL) 20 August 1985 (1985-08-20) the whole document	1-10
X	US 4 336 352 A (SAKURAI HISAYA ET AL) 22 June 1982 (1982-06-22) the whole document	1-10
A	US 6 242 548 B1 (KASPAR HARALD ET AL) 5 June 2001 (2001-06-05) the whole document	1-10
	----- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

25 March 2004

Date of mailing of the international search report

01/04/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Van Golde, L

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 603 935 A (SOLVAY) 29 June 1994 (1994-06-29) cited in the application the whole document -----	1-10

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 19945980	A	29-03-2001	DE	19945980 A1	29-03-2001
			AT	244264 T	15-07-2003
			AU	769434 B2	29-01-2004
			AU	7001700 A	30-04-2001
			BR	0014232 A	04-06-2002
			CA	2387708 A1	05-04-2001
			CN	1376170 T	23-10-2002
			DE	50002772 D1	07-08-2003
			WO	0123446 A1	05-04-2001
			EP	1228101 A1	07-08-2002
			JP	2003510429 T	18-03-2003
US 4536550	A	20-08-1985	JP	1012777 B	02-03-1989
			JP	1612249 C	30-07-1991
			JP	59196345 A	07-11-1984
			JP	1012778 B	02-03-1989
			JP	1612250 C	30-07-1991
			JP	59196346 A	07-11-1984
			JP	60036546 A	25-02-1985
			JP	1012781 B	02-03-1989
			JP	1612255 C	30-07-1991
			JP	60036547 A	25-02-1985
			CA	1218181 A1	17-02-1987
			DE	3470168 D1	05-05-1988
			EP	0129312 A1	27-12-1984
US 4336352	A	22-06-1982	JP	1282819 C	27-09-1985
			JP	56032506 A	02-04-1981
			JP	59010724 B	10-03-1984
			BE	884866 A1	16-12-1980
			BR	8005307 A	04-03-1981
			CA	1138148 A1	21-12-1982
			DE	3031540 A1	09-04-1981
			FR	2463791 A1	27-02-1981
			GB	2056996 A ,B	25-03-1981
			IT	1193551 B	08-07-1988
			NL	8004745 A ,C	26-02-1981
US 6242548	B1	05-06-2001	AU	6044399 A	05-12-2000
			CA	2372222 A1	23-11-2000
			EP	1185583 A1	13-03-2002
			WO	0069969 A1	23-11-2000
EP 0603935	A	29-06-1994	BE	1006439 A3	30-08-1994
			AT	191724 T	15-04-2000
			AU	670976 B2	08-08-1996
			AU	5249693 A	30-06-1994
			BR	9305106 A	28-06-1994
			CZ	9302853 A3	13-07-1994
			DE	69328345 D1	18-05-2000
			DE	69328345 T2	07-12-2000
			EP	1364971 A2	26-11-2003
			EP	0603935 A1	29-06-1994
			EP	0940411 A2	08-09-1999
			ES	2147192 T3	01-09-2000
			FI	935772 A	22-06-1994
			GR	3033922 T3	30-11-2000
			HU	66491 A2	28-11-1994

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0603935	A	NO 934729 A	22-06-1994
		PL 301589 A1	27-06-1994
		PT 603935 T	31-10-2000
		US 6344522 B1	05-02-2002
		US 6407185 B1	18-06-2002
		US 6136924 A	24-10-2000
		ZA 9309588 A	11-08-1994
<hr/>			